

Active compound combinations having insecticidal properties

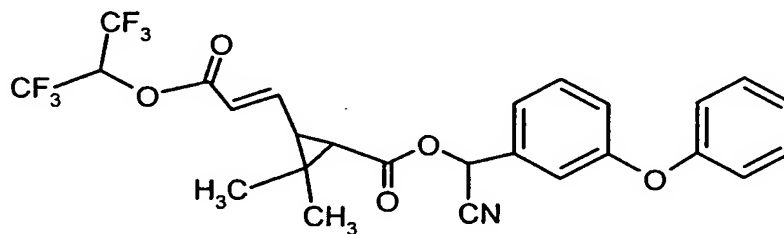
The present invention relates to novel active compound combinations comprising, firstly, triflumuron and, secondly, further known insecticidally active compounds, which combinations are highly suitable for controlling animal pests.

It is already known that triflumuron has insecticidal properties (DE-A 02 60 1780).

- 5 Furthermore, it is already known that pyrethroids have insecticidal properties (cf. WO 93-22 297, WO 93-10 083, DE-A 2 641 343, EP-A-347 488, EP-A-210 487, US-A 3 264 177 and EP-A-234 045). However, the activity of these compounds is not always satisfactory.

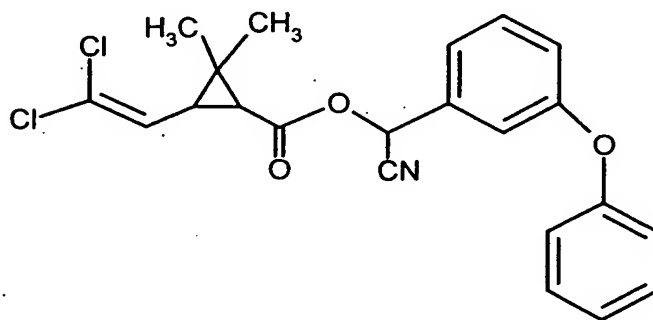
It has now been found that triflumuron and pyrethroids, preferably

1. acrinathrin



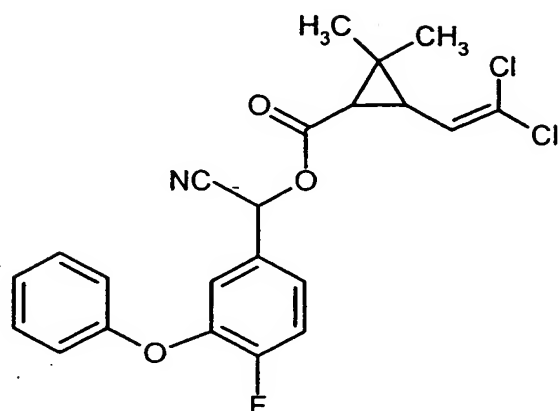
10 known from EP-A-048 186
and/or

2. alpha-cypermethrin



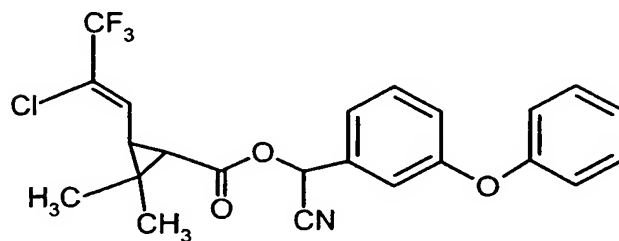
15 known from EP-A-067 461
and/or

3. betacyfluthrin



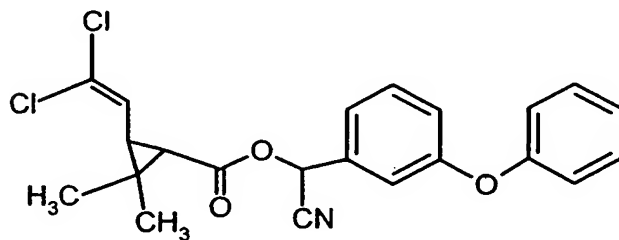
known from EP-A-206 149
and/or

5 4. cyhalothrin



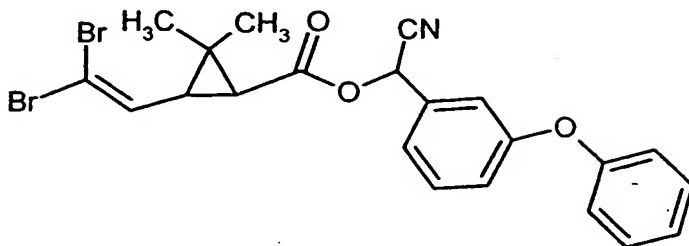
known from DE-A-2 802 962
and/or

5. cypermethrin



known from DE-A-2 326 077
and/or

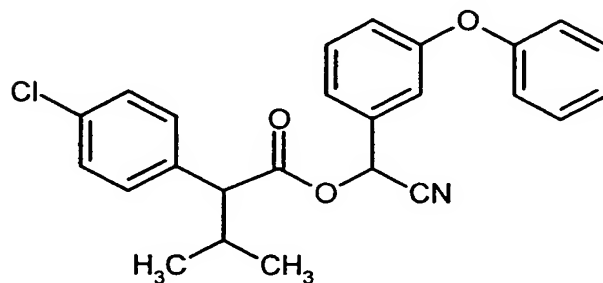
6. deltamethrin



known from DE-A-2 326 077

and/or

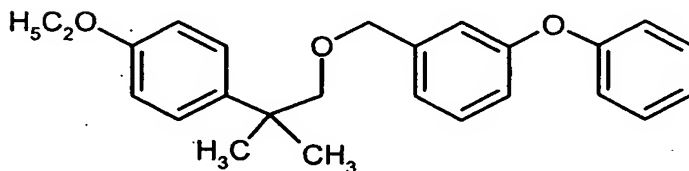
5 7. esfenvalerate



known from DE-A-2 737 297

and/or

8. ethofenprox

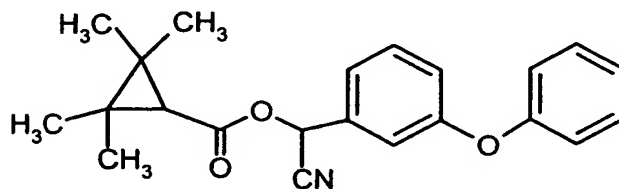


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known from DE-A-3 117 510

and/or

9. fenpropathrin

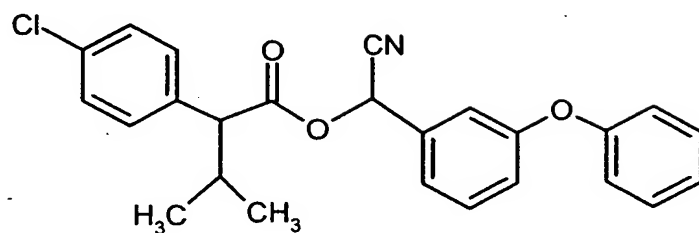


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known from DE-A-2 231 312

and/or

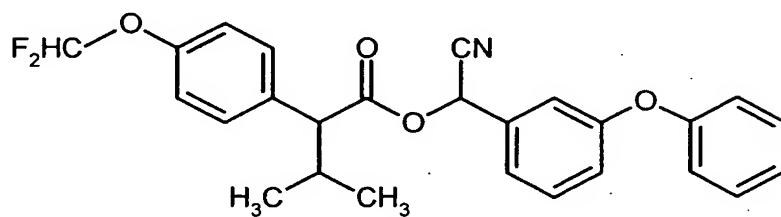
10. fenvalerate



known from DE-A-2 335 347

and/or

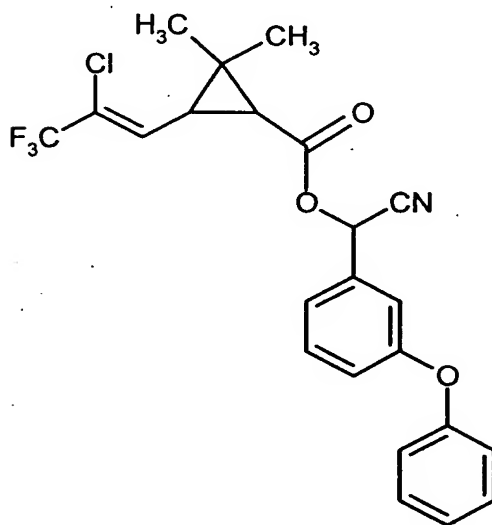
5 11. flucythrinate



known from DE-A-2 757 066

and/or

12. lambda-cyhalothrin

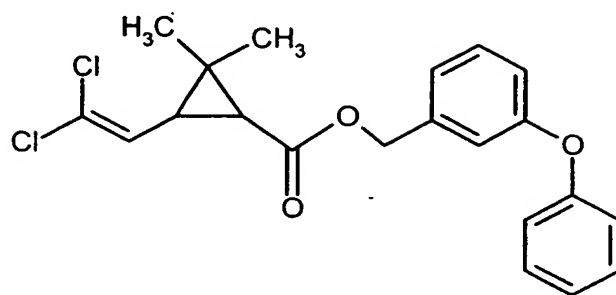


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known from EP-A-106 469

and/or

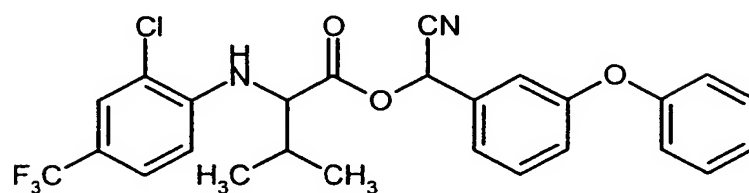
13. permethrin



known from DE-A-2 326 077

and/or

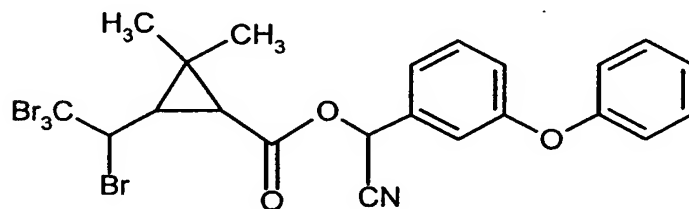
5 14. taufluvalinate



known from EP-A-038 617

and/or

15. tralomethrin

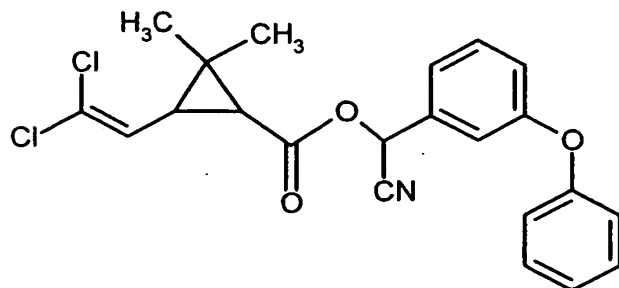


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known from DE-A-2 742 546

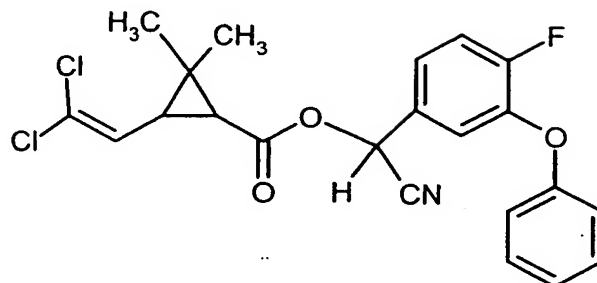
and/or

16. zeta-cypermethrin



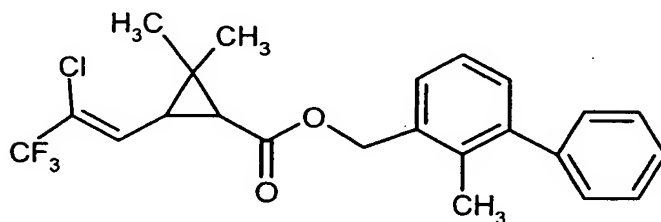
known from EP-A-026 542
and/or

17. cyfluthrin



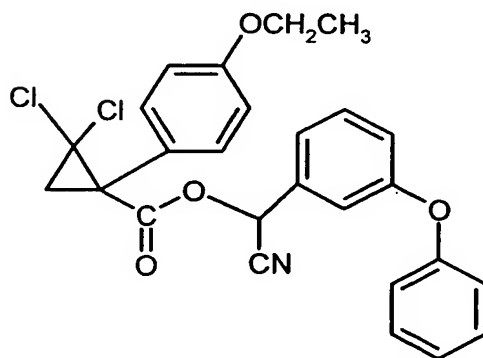
5 known from DE-A-27 09 264
and/or

18. bifenthrin



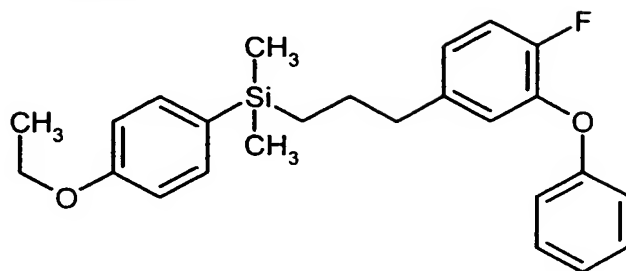
10 known from EP-A-049 977
and/or

19. cycloprothrin



known from DE-A-2653189
and/or

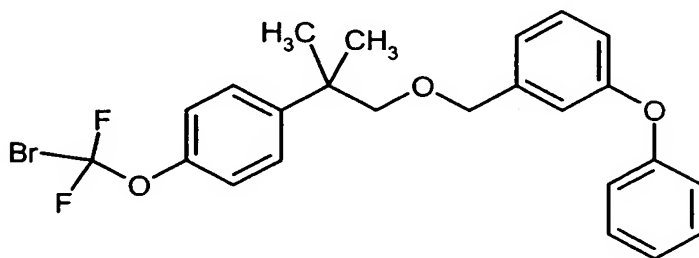
20. eflusilanate



known from DE-A-36 04 781

and/or

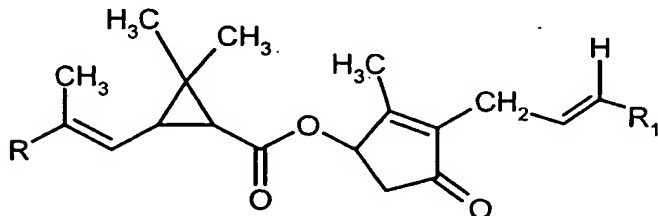
5 21. fubfenprox



known from DE-A-37 08 231

and/or

22. pyrethrin



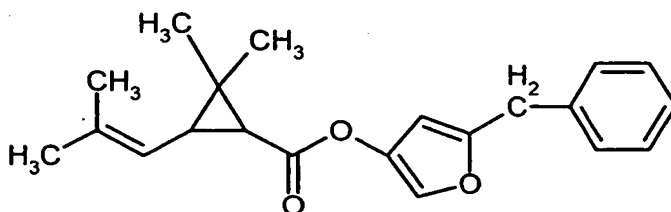
10

R = -CH₃ or -CO₂CH₃R₁ = -CH=CH₂ or -CH₃ or -CH₂CH₃

known from The Pesticide Manual, 1997, 11th Edition, p. 1056

and/or

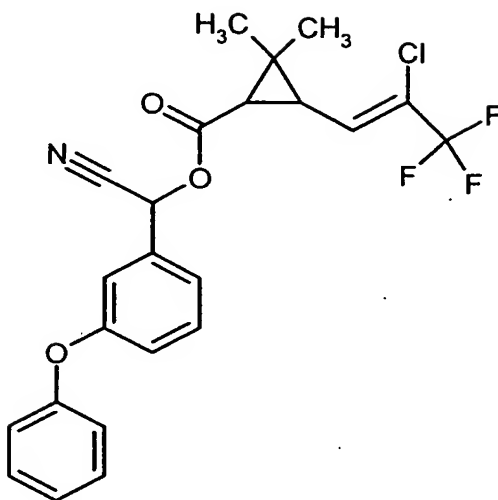
15 23. resmethrin



known from GB-A-1 168 797

and/or

24. gamma-cyhalothrin



known from GB-A-2 143 823

- 5 have very good insecticidal properties.

The following pyrethroids are particularly preferred:

acrinathrin, beta-cyfluthrin, cyhalothrin, lambda-cyhalothrin, tau-fluvalinate, tralomethrin, zeta-cypermethrin, cyfluthrin, bifenthrin, cycloprothrin, eflusilanate, fubfenprox, pyrethrin, resmethrin, gamma-cyhalothrin.

- 10 Very particular preference is given to betacyfluthrin. Especially preferred is lambda-cyhalothrin.

Surprisingly, the insecticidal activity of the active compound combination according to the invention is considerably higher than the sum of the activities of the individual active compounds. An unforeseeable true synergistic effect is present, and not just an addition of activities.

- 15 In addition to triflumuron, the active compound combinations according to the invention comprise at least one active compound of compounds 1 to 24.

In addition, the active compound combinations may also comprise further fungicidally, acaricidally or insecticidally effective additives.

- 20 If the active compounds in the active compound combinations according to the invention are present in certain weight ratios, the synergistic effect is particularly pronounced. However, the weight ratios of the active compounds in the active compound combinations can be varied within a

relatively wide range. In general, the combinations according to the invention comprise triflumuron and the mixing partner in the preferred and particularly preferred mixing ratios given in the table below:

- * the mixing ratios are based on weight ratios. The ratio is to be understood as meaning
5 triflumuron: mixing partner

Mixing partner	preferred mixing ratio	particularly preferred mixing ratio
acrinathrin	25:1 to 1:50	10:1 to 1:1
alpha-cypermethrin	50:1 to 1:5	10:1 to 1:1
betacyfluthrin	50:1 to 1:5	25:1 to 1:1
cyhalothrin	50:1 to 1:5	10:1 to 1:1
cypermethrin	50:1 to 1:5	10:1 to 1:1
deltamethrin	50:1 to 1:5	25:1 to 1:1
esfenvalerate	50:1 to 1:5	10:1 to 1:1
etofenprox	25:1 to 1:25	5:1 to 1:5
fenpropathrin	25:1 to 1:25	5:1 to 1:5
fenvalerate	25:1 to 1:25	10:1 to 1:1
flucythrinate	50:1 to 1:5	10:1 to 1:1
lambda-cyhalothrin	50:1 to 1:5	25:1 to 1:1
permethrin	50:1 to 1:10	25:1 to 1:5
tau-fluvalinate	20:1 to 1:5	10:1 to 1:2
tralomethrin	50:1 to 1:5	10:1 to 1:1
zeta-cypermethrin	50:1 to 1:5	10:1 to 1:2
cyfluthrin	50:1 to 1:5	10:1 to 1:1
bifenthrin	25:1 to 1:25	10:1 to 1:1
cycloprothrin	25:1 to 1:25	5:1 to 1:5
eflusanate	25:1 to 1:25	5:1 to 1:5
fubfenprox	25:1 to 1:25	5:1 to 1:5
pyrethrin	50:1 to 1:10	5:1 to 1:1
resmethrin	50:1 to 1:10	5:1 to 1:1
gamma-cyhalothrin	50:1 to 1:5	25:1 to 1:1

The active compound combinations according to the invention are suitable for controlling animal pests, preferably arthropods and nematodes, in particular insects and arachnids, found in agriculture, in animal health, in forests, in the protection of stored products and materials and in the
10 hygiene sector. They are active against normally sensitive and resistant species, and against all or individual developmental stages. The abovementioned pests include:

From the order of the Isopoda, for example, *Oniscus asellus*, *Armadillidium vulgare*, *Porcellio scaber*.

From the order of the Diplopoda, for example, *Blaniulus guttulatus*.

5

From the order of the Chilopoda, for example, *Geophilus carpophagus*, *Scutigera* spp.

From the order of the Symphyla, for example, *Scutigera* spp.

10 From the order of the Thysanura, for example, *Lepisma saccharina*.

From the order of the Collembola, for example, *Onychiurus armatus*.

15 From the order of the Orthoptera, for example, *Acheta domesticus*, *Gryllotalpa* spp., *Locusta migratoria migratorioides*, *Melanoplus* spp., *Schistocerca gregaria*.

From the order of the Blattaria, for example, *Blatta orientalis*, *Periplaneta americana*, *Leucophaea maderae*, *Blattella germanica*.

20 From the order of the Dermaptera, for example, *Forficula auricularia*.

From the order of the Isoptera, for example, *Reticulitermes* spp.

25 From the order of the Phthiraptera, for example, *Pediculus humanus corporis*, *Haematopinus* spp., *Linognathus* spp., *Trichodectes* spp., *Damalinia* spp.

From the order of the Thysanoptera, for example, *Hercinothrips femoralis*, *Thrips tabaci*, *Thrips palmi*, *Frankliniella occidentalis*.

30 From the order of the Heteroptera, for example, *Eurygaster* spp., *Dysdercus intermedius*, *Piesma quadrata*, *Cimex lectularius*, *Rhodnius prolixus*, *Triatoma* spp.

35 From the order of the Homoptera, for example, *Aleurodes brassicae*, *Bemisia tabaci*, *Trialeurodes vaporariorum*, *Aphis gossypii*, *Brevicoryne brassicae*, *Cryptomyzus ribis*, *Aphis fabae*, *Aphis pomi*, *Eriosoma lanigerum*, *Hyalopterus arundinis*, *Phylloxera vastatrix*, *Pemphigus* spp., *Macrosiphum avenae*, *Myzus* spp., *Phorodon humuli*, *Rhopalosiphum padi*, *Empoasca* spp., *Euscelis bilobatus*,

Nephotettix cincticeps, *Lecanium corni*, *Saissetia oleae*, *Laodelphax striatellus*, *Nilaparvata lugens*, *Aonidiella aurantii*, *Aspidiotus hederae*, *Pseudococcus* spp., *Psylla* spp.

From the order of the Lepidoptera, for example, *Pectinophora gossypiella*, *Bupalus piniarius*,
 5 *Cheimatobia brumata*, *Lithocolletis blancardella*, *Hyponomeuta padella*, *Plutella xylostella*,
Malacosoma neustria, *Euproctis chrysorrhoea*, *Lymantria* spp., *Bucculatrix thurberiella*,
Phyllocnistis citrella, *Agrotis* spp., *Euxoa* spp., *Feltia* spp., *Earias insulana*, *Heliothis* spp.,
Mamestra brassicae, *Panolis flammea*, *Spodoptera* spp., *Trichoplusia ni*, *Carpocapsa pomonella*,
Pieris spp., *Chilo* spp., *Pyrausta nubilalis*, *Ephestia kuehniella*, *Galleria mellonella*, *Tineola*
 10 *bisselliella*, *Tinea pellionella*, *Hofmannophila pseudospretella*, *Cacoecia podana*, *Capua reticulana*,
Choristoneura fumiferana, *Clysia ambiguella*, *Homona magnanima*, *Tortrix viridana*,
Cnaphalocerus spp., *Oulema oryzae*.

From the order of the Coleoptera, for example, *Anobium punctatum*, *Rhizopertha dominica*,
 15 *Bruchidius obtectus*, *Acanthoscelides obtectus*, *Hylotrupes bajulus*, *Agelastica alni*, *Leptinotarsa*
decmilineata, *Phaedon cochleariae*, *Diabrotica* spp., *Psylliodes chrysocephala*, *Epilachna*
varivestis, *Atomaria* spp., *Oryzaephilus surinamensis*, *Anthonomus* spp., *Sitophilus* spp.,
Otiorrhynchus sulcatus, *Cosmopolites sordidus*, *Ceuthorrhynchus assimilis*, *Hypera postica*,
Dermestes spp., *Trogoderma* spp., *Anthrenus* spp., *Attagenus* spp., *Lyctus* spp., *Meligethes aeneus*,
 20 *Ptinus* spp., *Niptus hololeucus*, *Gibbium psylloides*, *Tribolium* spp., *Tenebrio molitor*, *Agriotes*
spp., *Conoderus* spp., *Melolontha melolontha*, *Amphimallon solstitialis*, *Costelytra zealandica*,
Lissorhoptrus oryzophilus.

From the order of the Hymenoptera, for example, *Diprion* spp., *Hoplocampa* spp., *Lasius* spp.,
 25 *Monomorium pharaonis*, *Vespa* spp.

From the order of the Diptera, for example, *Aedes* spp., *Anopheles* spp., *Culex* spp., *Drosophila*
melanogaster, *Musca* spp., *Fannia* spp., *Calliphora erythrocephala*, *Lucilia* spp., *Chrysomyia* spp.,
Cuterebra spp., *Gastrophilus* spp., *Hyppobosca* spp., *Stomoxys* spp., *Oestrus* spp., *Hypoderma* spp.,
 30 *Tabanus* spp., *Tannia* spp., *Bibio hortulanus*, *Oscinella frit*, *Phorbia* spp., *Pegomyia hyoscyami*,
Ceratitis capitata, *Dacus oleae*, *Tipula paludosa*, *Hylemyia* spp., *Liriomyza* spp.

From the order of the Siphonaptera, for example, *Xenopsylla cheopis*, *Ceratophyllus* spp.

35 From the class of the Arachnida, for example, *Scorpio maurus*, *Latrodectus mactans*, *Acarus siro*,
Argas spp., *Ornithodoros* spp., *Dermanyssus gallinae*, *Eriophyes ribis*, *Phyllocoptura oleivora*,
Boophilus spp., *Rhipicephalus* spp., *Amblyomma* spp., *Hyalomma* spp., *Ixodes* spp., *Psoroptes*

spp., Chorioptes spp., Sarcoptes spp., Tarsonemus spp., Bryobia praetiosa, Panonychus spp., Tetranychus spp., Hemitarsonemus spp., Brevipalpus spp.

The plant-parasitic nematodes include, for example, Pratylenchus spp., Radopholus similis,
5 Ditylenchus dipsaci, Tylenchulus semipenetrans, Heterodera spp., Globodera spp., Meloidogyne
spp., Aphelenchoides spp., Longidorus spp., Xiphinema spp., Trichodorus spp., Bursaphelenchus
spp.

The active compound combinations can be converted into the customary formulations such as
10 solutions, emulsions, wettable powders, suspensions, powders, dusts, pastes, soluble powders,
granules, suspension-emulsion concentrates, natural and synthetic materials impregnated with
active compound, and microencapsulations in polymeric materials.

These formulations are produced in a known manner, for example by mixing the active compounds
15 with extenders, that is, liquid solvents and/or solid carriers, optionally with the use of surfactants,
that is, emulsifiers and/or dispersants, and/or foam formers.

If the extender used is water, it is also possible, for example, to use organic solvents as cosolvents.
The following are essentially suitable as liquid solvents: aromatics such as xylene, toluene or
20 alkyl-naphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as
chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as
cyclohexane or paraffins, for example mineral oil fractions, mineral and vegetable oils, alcohols
such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone,
methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide and
25 dimethyl sulfoxide, or else water.

Suitable solid carriers are:

for example ammonium salts and ground natural minerals such as kaolins, clays, talc, chalk, quartz,
30 attapulgite, montmorillonite or diatomaceous earth, and ground synthetic materials such as highly
disperse silica, alumina and silicates; suitable solid carriers for granules are: for example crushed
and fractionated natural rocks such as calcite, marble, pumice, sepiolite and dolomite, or else
synthetic granules of inorganic and organic meals, and granules of organic material such as
sawdust, coconut shells, corn cobs and tobacco stalks; suitable emulsifiers and/or foam formers are:
35 for example nonionic and anionic emulsifiers such as polyoxyethylene fatty acid esters,
polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulfonates, alkyl

sulfates, arylsulfonates, or else protein hydrolysates; suitable dispersants are: for example lignosulfite waste liquors and methylcellulose.

5 Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other possible additives are mineral and vegetable oils.

10 It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic colorants such as alizarin colorants, azo colorants and metal phthalocyanine colorants, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

15 The formulations generally comprise between 0.1 and 95% by weight of active compound, preferably between 0.5 and 90%.

20 The active compound combinations according to the invention can be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with other active compounds, such as insecticides, attractants, sterilants, bactericides, acaricides, nematocides, fungicides, growth-regulating substances or herbicides. The insecticides include, for example, phosphates, carbamates, carboxylates, chlorinated hydrocarbons, phenylureas and substances produced by microorganisms, inter alia.

25 A mixtures with other known active compounds such as herbicides or with fertilizers and growth regulators is also possible.

30 When used as insecticides, the active compound combinations according to the invention can furthermore be present in their commercially available formulations and in the use forms, prepared from these formulations, as a mixture with synergists. Synergists are compounds which increase the action of the active compounds, without it being necessary for the synergist added to be active itself.

35 The active compound content of the use forms prepared from the commercially available formulations can vary within wide limits. The active compound concentration of the use forms can be from 0.0000001 to 95% by weight of active compound, preferably between 0.0001 and 1% by weight.

The compounds are employed in a customary manner appropriate for the use forms.

When used against hygiene pests and stored-product pests, the active compound combinations are distinguished by an excellent residual action on wood and clay as well as good stability to alkali on
5 limed substrates.

The active compound combinations according to the invention are not only active against plant pests, hygiene pests and stored-product pests, but also, in the veterinary medicine sector, against animal parasites (ectoparasites) such as hard ticks, soft ticks, mange mites, harvest mites, flies
10 (stinging and licking), parasitizing fly larvae, lice, head lice, bird lice and fleas. These parasites include:

From the order of the Anoplurida, for example, *Haematopinus* spp., *Linognathus* spp., *Pediculus* spp., *Phtirus* spp., *Solenopotes* spp.
15

From the order of the Mallophagida and the suborders Amblycerina and Ischnocerina, for example, *Trimenopon* spp., *Menopon* spp., *Trinoton* spp., *Bovicola* spp., *Werneckiella* spp., *Lepikentron* spp., *Damalina* spp., *Trichodectes* spp., *Felicola* spp.

20 From the order Diptera and the suborders Nematocerina and Brachycerina, for example, *Aedes* spp., *Anopheles* spp., *Culex* spp., *Simulium* spp., *Eusimulium* spp., *Phlebotomus* spp., *Lutzomyia* spp., *Culicoides* spp., *Chrysops* spp., *Hybomitra* spp., *Atylotus* spp., *Tabanus* spp., *Haematopota* spp., *Philipomyia* spp., *Braula* spp., *Musca* spp., *Hydrotaea* spp., *Stomoxys* spp., *Haematobia* spp., *Morellia* spp., *Fannia* spp., *Glossina* spp., *Calliphora* spp., *Lucilia* spp., *Chrysomyia* spp.,
25 *Wohlfahrtia* spp., *Sarcophaga* spp., *Oestrus* spp., *Hypoderma* spp., *Gasterophilus* spp., *Hippobosca* spp., *Lipoptena* spp., *Melophagus* spp.

From the order of the Siphonaptera, for example, *Pulex* spp., *Ctenocephalides* spp., *Xenopsylla* spp., *Ceratophyllus* spp.
30

From the order of the Heteroptera, for example, *Cimex* spp., *Triatoma* spp., *Rhodnius* spp., *Panstrongylus* spp.

From the order of the Blattellidae, for example, *Blattella orientalis*, *Periplaneta americana*, *Blattella germanica*, *Supella* spp.
35

From the subclass of the Acaria (Acarida) and the orders of the Meta- and Mesostigmata, for example, Argas spp., Ornithodoros spp., Otobius spp., Ixodes spp., Amblyomma spp., Boophilus spp., Dermacentor spp., Haemophysalis spp., Hyalomma spp., Rhipicephalus spp., Dermanyssus spp., Raillietia spp., Pneumonyssus spp., Sternostoma spp., Varroa spp.

5

From the order of the Actinedida (Prostigmata) and Acaridida (Astigmata), for example, Acarapis spp., Cheyletiella spp., Ornithocheyletia spp., Myobia spp., Psorergates spp., Demodex spp., Trombicula spp., Listrophorus spp., Acarus spp., Tyrophagus spp., Caloglyphus spp., Hypodectes spp., Pterolichus spp., Psoroptes spp., Chorioptes spp., Otodectes spp., Sarcoptes spp., Notoedres spp., Knemidocoptes spp., Cytodites spp., Laminosioptes spp.

10

The active compound combinations according to the invention are also suitable for controlling arthropods which attack agricultural livestock such as, for example, cattle, sheep, goats, horses, pigs, donkeys, camels, buffaloes, rabbits, chickens, turkeys, ducks, geese, honey-bees, other domestic animals such as, for example, dogs, cats, caged birds, aquarium fish and so-called experimental animals such as, for example, hamsters, guinea pigs, rats and mice. By controlling these arthropods, cases of death and reductions in productivity (for meat, milk, wool, hides, eggs, honey and the like) should be diminished, so that more economical and simpler animal husbandry is possible by the use of the active compound combinations according to the invention.

20

The active compound combinations according to the invention are used in the veterinary sector in a known manner by enteral administration in the form of, for example, tablets, capsules, potions, drenches, granules, pastes, boluses, the feed-through method, suppositories, by parenteral administration such as, for example, by injections (intramuscularly, subcutaneously, intravenously, intraperitoneally and the like), implants, by nasal administration, by dermal administration in the form of, for example, immersing or dipping, spraying, pouring-on, spotting-on, washing, dusting, and with the aid of active-compound-comprising molded articles such as collars, ear tags, tail tags, limb bands, halters, marking devices and the like.

25

When used for cattle, poultry, domestic animals and the like, the active compound combinations can be applied as formulations (for example powders, emulsions, flowables) comprising the active compounds in an amount of 1 to 80% by weight, either directly or after 100- to 10 000-fold dilution, or they may be used as a chemical dip.

30

35

Moreover, it has been found that the active compound combinations according to the invention show a potent insecticidal action against insects which destroy industrial materials.

The following insects may be mentioned by way of example and with preference, but not by way of limitation:

Beetles such as

- 5 Hylotrupes bajulus, Chlorophorus pilosis, Anobium punctatum, Xestobium rufovillosum, Ptilinus pecticornis, Dendrobium pertinex, Ernobius mollis, Priobium carpini, Lyctus brunneus, Lyctus africanus, Lyctus planicollis, Lyctus linearis, Lyctus pubescens, Trogoxylon aequale, Minthes rugicollis, Xyleborus spec., Tryptodendron spec., Apate monachus, Bostrychus capucins, Heterobostrychus brunneus, Sinoxylon spec., Dinoderus minutus.

10

Dermapterans such as

Sirex juvenicus, Urocerus gigas, Urocerus gigas taignus, Urocerus augur.

Termites such as

- 15 Kaloterms flavicollis, Cryptoterms brevis, Heteroterms indicola, Reticulitermes flavipes, Reticulitermes santonensis, Reticulitermes lucifugus, Mastoterms darwiniensis, Zootermopsis nevadensis, Coptoterms formosanus.

Bristle-tails such as Lepisma saccharina.

20

Industrial materials in the present context are understood as meaning non-living materials such as, preferably, polymers, adhesives, glues, paper and board, leather, wood, timber products and paints.

- 25 The material which is to be protected from insect attack is very particularly preferably wood and timber products.

Wood and timber products which can be protected by the composition according to the invention, or mixtures comprising it, are to be understood as meaning, for example:

- 30 Construction timber, wooden beams, railway sleepers, bridge components, jetties, vehicles made of wood, boxes, pallets, containers, telephone poles, wood lagging, windows and doors made of wood, plywood, chipboard, joinery, or timber products which quite generally are used in house construction or building joinery.

- 35 The active compound combinations can be used as such, in the form of concentrates or generally customary formulations such as powders, granules, solutions, suspensions, emulsions or pastes.

The abovementioned formulations can be prepared in a manner known per se, for example by mixing the active compounds with at least one solvent or diluent, emulsifier, dispersant and/or binder or fixative, water repellent, if desired desiccants and UV stabilizers, and if desired colorants and pigments and other processing auxiliaries.

5

The insecticidal compositions or concentrates used for protecting wood and timber products comprise the active compound according to the invention in a concentration of 0.0001 to 95% by weight, in particular 0.001 to 60% by weight.

- 10 The amount of composition or concentrate employed depends on the species and the abundance of the insects and on the medium. The optimal quantity to be employed can be determined in each case by test series upon application. In general, however, it will suffice to employ 0.0001 to 20% by weight, preferably 0.001 to 10% by weight, of the active compound, based on the material to be protected.

15

A suitable solvent and/or diluent is an organochemical solvent or solvent mixture and/or an oily or oil-type organochemical solvent or solvent mixture of low volatility and/or a polar organochemical solvent or solvent mixture and/or water and, if appropriate, an emulsifier and/or wetter.

- 20 Organochemical solvents which are preferably employed are oily or oil-type solvents with an evaporation number of above 35 and a flash point of above 30°C, preferably above 45°C. Such oily and oil-type solvents which are insoluble in water and of low volatility and which are used are suitable mineral oils or their aromatic fractions or mineral-oil-containing solvent mixtures, preferably white spirit, petroleum and/or alkylbenzene.

- 25 Mineral oils with a boiling range of 170 to 220°C, white spirit with a boiling range of 170 to 220°C, spindle oil with a boiling range of 250 to 350°C, petroleum and aromatics with a boiling range of 160 to 280°C, oil of turpentine, and the like are advantageously used.

- 30 In a preferred embodiment, liquid aliphatic hydrocarbons with a boiling range of 180 to 210°C or high-boiling mixtures of aromatic and aliphatic hydrocarbons with a boiling range of 180 to 220°C and/or spindle oil and/or monochloronaphthalene, preferably α -monochloronaphthalene, are used.

- 35 The organic oily or oil-type solvents of low volatility and with an evaporation number of above 35 and a flash point of above 30°C, preferably above 45°C, can be replaced in part by organochemical solvents of high or medium volatility, with the proviso that the solvent mixture also has an

evaporation number of above 35 and a flash point of above 30°C, preferably above 45°C, and that the mixture is soluble or emulsifiable in this solvent mixture.

In a preferred embodiment, some of the organochemical solvent or solvent mixture or an aliphatic polar organochemical solvent or solvent mixture is replaced. Aliphatic organochemical solvents which contain hydroxyl and/or ester and/or ether groups are preferably used, such as, for example, glycol ethers, esters or the like.

Organochemical binders used for the purposes of the present invention are the synthetic resins and/or binding drying oils which are known per se and which can be diluted in water and/or dissolved or dispersed or emulsified in the organochemical solvents employed, in particular binders composed of, or comprising, an acrylate resin, a vinyl resin, for example polyvinyl acetate, polyester resin, polycondensation or polyaddition resin, polyurethane resin, alkyd resin or modified alkyd resin, phenol resin, hydrocarbon resin such as indene/coumarone resin, silicone resin, drying vegetable and/or drying oils and/or physically drying binders based on a natural and/or synthetic resin.

The synthetic resin employed as binder can be employed in the form of an emulsion, dispersion or solution. Bitumen or bituminous substances may also be used as binders, in amounts of up to 10% by weight. In addition, colorants, pigments, water repellants, odor-masking agents, and inhibitors or anticorrosive agents and the like, all of which are known per se, can be employed.

In accordance with the invention, the composition or the concentrate preferably comprises, as organochemical binders, at least one alkyd resin or modified alkyd resin and/or a drying vegetable oil. Alkyd resins which are preferably used in accordance with the invention are those with an oil content of over 45% by weight, preferably 50 to 68% by weight.

Some or all of the abovementioned binder can be replaced by a fixative (mixture) or plasticizer (mixture). These additives are intended to prevent volatilization of the active compounds, and also crystallization or precipitation. They preferably replace 0.01 to 30% of the binder (based on 100% of binder employed).

The plasticizers are from the chemical classes of the phthalic esters, such as dibutyl phthalate, dioctyl phthalate or benzyl butyl phthalate, phosphoric esters such as tributyl phosphate, adipic esters such as di(2-ethylhexyl) adipate, stearates such as butyl stearate or amyl stearate, oleates such as butyl oleate, glycerol ethers or higher-molecular-weight glycol ethers, glycerol esters and p-toluenesulfonic esters.

Fixatives are based chemically on polyvinyl alkyl ethers such as, for example, polyvinyl methyl ether, or ketones such as benzophenone and ethylenebenzophenone.

- 5 Other suitable solvents or diluents are, in particular, water, if appropriate as a mixture with one or more of the abovementioned organochemical solvents or diluents, emulsifiers and dispersants.

Particularly effective timber protection is achieved by industrial-scale impregnating processes, for example the vacuum, double-vacuum or pressure processes.

10

The active compound combinations according to the invention can equally be employed for protecting objects which come into contact with saltwater or brackish water, in particular hulls, screens, nets, buildings, quaysides and signaling systems, against fouling.

- 15 Fouling by sessile Oligochaeta, such as Serpulidae, and by shells and species from the Ledamorpha group (goose barnacles), such as various Lepas and Scalpellum species, or by species from the Balanomorpha group (acorn barnacles), such as Balanus or Pollicipes species, increases the frictional drag of ships and, as a consequence, leads to a marked increase in operation costs owing to higher energy consumption and additionally frequent stops in the dry dock.

20

Apart from fouling by algae, for example Ectocarpus sp. and Ceramium sp., in particular fouling by sessile Entomostraka groups, which come under the generic term Cirripedia (cirriped crustaceans), is of particular importance.

- 25 Surprisingly, it has now been found that the active compound combinations according to the invention have an outstanding antifouling action.

- Use of the active compound combinations according to the invention allows the use of heavy metals such as, for example, in bis(trialkyltin) sulfides, tri-*n*-butyltin laurate, tri-*n*-butyltin chloride, 30 copper(I) oxide, triethyltin chloride, tri-*n*-butyl(2-phenyl-4-chlorophenoxy)tin, tributyltin oxide, molybdenum disulfide, antimony oxide, polymeric butyl titanate, phenyl (bispyridine)bismuth chloride, tri-*n*-butyltin fluoride, manganese ethylenebisthiocarbamate, zinc dimethyldithiocarbamate, zinc ethylenebisthiocarbamate, zinc salts and copper salts of 2-pyridinethiol 1-oxide, bisdimethyldithiocarbamoylzinc ethylenebisthiocarbamate, zinc oxide, 35 copper(I) ethylenebisdithiocarbamate, copper thiocyanate, copper naphthenate and tributyltin halides to be dispensed with, or the concentration of these compounds to be substantially reduced.

If appropriate, the ready-to-use antifouling paints can additionally comprise other active compounds, preferably algicides, fungicides, herbicides, molluscicides, or other antifouling active compounds.

- 5 Preferable suitable components in combinations for the antifouling compositions according to the invention are:

algicides such as

- 2-*tert*-butylamino-4-cyclopropylamino-6-methylthio-1,3,5-triazine, dichlorophen, diuron, endothal,
10 fentin acetate, isoproturon, methabenzthiazuron, oxyfluorfen, quinoclamine and terbutryn;

fungicides such as

- benzo[*b*]thiophenecarboxylic acid cyclohexylamide S,S-dioxide, dichlofluanid, fluorfolpet, 3-iodo-
2-propynyl butylcarbamate, tolylfluanid and azoles such as azaconazole, cyproconazole,
15 epoxyconazole, hexaconazole, metconazole, propiconazole and tebuconazole;

molluscicides such as

fentin acetate, metaldehyde, methiocarb, niclosamid, thiodicarb and trimethacarb;

- 20 or conventional antifouling active compounds such as

- 4,5-dichloro-2-octyl-4-isothiazolin-3-one, diiodomethylparatryl sulfone, 2-(N,N-dimethyl-
thiocarbamoylthio)-5-nitrothiazyl, potassium salts, copper salts, sodium salts and zinc salts of
2-pyridinethiol 1-oxide, pyridine/triphenylborane, tetrabutyl-distannoxane, 2,3,5,6-tetrachloro-4-
(methylsulfonyl)pyridine, 2,4,5,6-tetrachloroisophthalonitrile, tetramethylthiuram disulfide and
25 2,4,6-trichlorophenylmaleimide.

The antifouling compositions used comprise the active compound combinations according to the invention in a concentration of 0.001 to 50% by weight, in particular 0.01 to 20% by weight.

- 30 Moreover, the antifouling compositions according to the invention comprise the customary components such as, for example, those described in Ungerer, *Chem. Ind.* 1985, 37, 730-732 and Williams, *Antifouling Marine Coatings*, Noyes, Park Ridge, 1973.

- Besides the algicidal, fungicidal, molluscicidal active compounds and insecticidal active
35 compounds according to the invention, antifouling paints comprise, in particular, binders.

Examples of recognized binders are polyvinyl chloride in a solvent system, chlorinated rubber in a solvent system, acrylic resins in a solvent system, in particular in an aqueous system, vinyl chloride/vinyl acetate copolymer systems in the form of aqueous dispersions or in the form of organic solvent systems, butadiene/styrene/acrylonitrile rubbers, drying oils such as linseed oil, resin esters or modified hardened resins in combination with tar or bitumen, asphalt and epoxy compounds, small amounts of chlorine rubber, chlorinated polypropylene and vinyl resins.

If appropriate, paints also comprise inorganic pigments, organic pigments or colorants which are preferably insoluble in seawater. Paints may furthermore comprise materials such as colophonium to allow controlled release of the active compounds. Furthermore, the paints may comprise plasticizers, modifiers which affect the rheological properties and other conventional constituents. The compounds according to the invention or the abovementioned mixtures may also be incorporated into self-polishing antifouling systems.

The active compound combinations are also suitable for controlling animal pests, in particular insects, arachnids and mites, which are found in enclosed spaces such as, for example, dwellings, factory halls, offices, vehicle cabins and the like. They can be employed in domestic insecticide products for controlling these pests. They are active against sensitive and resistant species and against all developmental stages. These pests include:

From the order of the Scorpionidea, for example, *Buthus occitanus*.

From the order of the Acarina, for example, *Argas persicus*, *Argas reflexus*, *Bryobia* spp., *Dermanyssus gallinae*, *Glyciphagus domesticus*, *Ornithodoros moubat*, *Rhipicephalus sanguineus*, *Trombicula alfreddugesi*, *Neutrombicula autumnalis*, *Dermatophagoides pteronissimus*, *Dermatophagoides farinae*.

From the order of the Araneae, for example, *Aviculariidae*, *Araneidae*.

From the order of the Opiliones, for example, *Pseudoscorpiones chelifer*, *Pseudoscorpiones cheiridium*, *Opiliones phalangium*.

From the order of the Isopoda, for example, *Oniscus asellus*, *Porcellio scaber*.

From the order of the Diplopoda, for example, *Blaniulus guttulatus*, *Polydesmus* spp.

From the order of the Chilopoda, for example, *Geophilus* spp.

From the order of the Zygentoma, for example, *Ctenolepisma* spp., *Lepisma saccharina*, *Lepismodes inquilinus*.

- 5 From the order of the Blattaria, for example, *Blatta orientalis*, *Blattella germanica*, *Blattella asahinai*, *Leucophaea maderae*, *Panchlora* spp., *Parcoblatta* spp., *Periplaneta australasiae*, *Periplaneta americana*, *Periplaneta brunnea*, *Periplaneta fuliginosa*, *Supella longipalpa*.

From the order of the Saltatoria, for example, *Acheta domesticus*.

10

From the order of the Dermaptera, for example, *Forficula auricularia*.

From the order of the Isoptera, for example, *Kaloterms* spp., *Reticulitermes* spp.

- 15 From the order of the Psocoptera, for example, *Lepinatus* spp., *Liposcelis* spp.

From the order of the Coleoptera, for example, *Anthrenus* spp., *Attagenus* spp., *Dermestes* spp., *Latheticus oryzae*, *Necrobia* spp., *Ptinus* spp., *Rhizopertha dominica*, *Sitophilus granarius*, *Sitophilus oryzae*, *Sitophilus zeamais*, *Stegobium paniceum*.

20

From the order of the Diptera, for example, *Aedes aegypti*, *Aedes albopictus*, *Aedes taeniorhynchus*, *Anopheles* spp., *Calliphora erythrocephala*, *Chrysozona pluvialis*, *Culex quinquefasciatus*, *Culex pipiens*, *Culex tarsalis*, *Drosophila* spp., *Fannia canicularis*, *Musca domestica*, *Phlebotomus* spp., *Sarcophaga carnaria*, *Simulium* spp., *Stomoxys calcitrans*, *Tipula paludosa*.

25

From the order of the Lepidoptera, for example, *Achroia grisella*, *Galleria mellonella*, *Plodia interpunctella*, *Tinea cloacella*, *Tinea pellionella*, *Tineola bisselliella*.

- 30 From the order of the Siphonaptera, for example, *Ctenocephalides canis*, *Ctenocephalides felis*, *Pulex irritans*, *Tunga penetrans*, *Xenopsylla cheopis*.

From the order of the Hymenoptera, for example, *Camponotus herculeanus*, *Lasius fuliginosus*, *Lasius niger*, *Lasius umbratus*, *Monomorium pharaonis*, *Paravespula* spp., *Tetramorium caespitum*.

35

From the order of the Anoplura, for example, *Pediculus humanus capitis*, *Pediculus humanus corporis*, *Phthirus pubis*.

From the order of the Heteroptera, for example, *Cimex hemipterus*, *Cimex lectularius*, *Rhodinus prolixus*, *Triatoma infestans*.

5 They are used as aerosols, pressureless spray products, for example pump and atomizer sprays, automatic fogging systems, foggers, foams, gels, evaporator products with evaporator tablets made of cellulose or polymer, liquid evaporators, gel and membrane evaporators, propeller-driven evaporators, energy-free, or passive, evaporation systems, moth papers, moth bags and moth gels, as granules or dusts, in baits for spreading or in bait stations.

10

According to the invention, it is possible to treat all plants and parts of plants. Plants are to be understood here as meaning all plants and plant populations such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional breeding and optimization methods or by biotechnological and genetic engineering methods or combinations of these methods, including the transgenic plants and including the plant cultivars which can or cannot be protected by plant breeders' certificates. Parts of plants are to be understood as meaning all above-ground and below-ground parts and organs of plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stems, trunks, flowers, fruit-bodies, fruits and seeds and also roots, tubers and rhizomes.

15 20 Parts of plants also include harvested plants and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings and seeds.

The treatment according to the invention of the plants and parts of plants with the active compounds is carried out directly or by action on their environment, habitat or storage area according to customary treatment methods, for example by dipping, spraying, evaporating, atomizing, broadcasting, brushing-on and, in the case of propagation material, in particular in the case of seeds, furthermore by one- or multi-layer coating.

25

The good insecticidal action of the active compound combinations according to the invention can be seen from the examples which follow. While the individual active compounds show weaknesses in their action, the combinations show an action which exceeds a simple sum of actions.

30

A synergistic effect in insecticides and acaricides is always present when the action of the active compound combinations exceeds the total of the actions of the active compounds when applied individually.

35

The expected action for a given combination of two active compounds can be calculated as follows, according to S.R. Colby, Weeds 15 (1967), 20-22:

If

5

X is the kill rate, expressed as a percentage of the untreated control, when employing active compound A at an application rate of m g/ha or in a concentration of m ppm,

10

Y is the kill rate, expressed as a percentage of the untreated control, when employing active compound B at an application rate of n g/ha or in a concentration of n ppm and

E is the kill rate, expressed as a percentage of the untreated control, when employing active compounds A and B at application rates of m and n g/ha or in a concentration of m and n ppm,

15

then

$$E = X + Y - \frac{X \cdot Y}{100}$$

20 If the actual insecticidal kill rate exceeds the calculated value, the kill of the combination is superadditive, i.e. a synergistic effect is present. In this case, the actually observed kill rate must exceed the value calculated using the above formula for the expected kill rate (E).

Example A

Heliothis armigera test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

- Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with caterpillars of the cotton bollworm
10 (*Heliothis armigera*) while the leaves are still moist.

After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed. The determined kill rates are entered into Colby's formula (see sheet 1).

- In this test, the following active compound combination in accordance with the present application
15 showed a synergistically enhanced activity compared to the active compounds applied on their own:

Table A

Plant-damaging insects
Heliothis armigera test

Active compound	Concentration in ppm	Kill in % after 6 ^d
triflumuron		
known	4	0
β-cyfluthrin		
known	0.16	65
triflumuron + β-cyfluthrin (25 : 1)		
according to the invention		
	4 + 0.16	<u>found</u> * <u>calc.</u> ** 80 65

* found = activity found

** calc. = activity calculated using Colby's formula

Table A

Plant-damaging insects
Heliothis armigera test

Active compound	Concentration in ppm	Kill in % after 3 ^d
triflumuron		
known	0.8	0
deltamethrin		
known	0.032	10
triflumuron + deltamethrin (25 : 1)		
according to the invention		
	0.8 + 0.032	<u>found</u> * <u>calc.</u> ** 30 10

* found = activity found

** calc. = activity calculated using Colby's formula

Table A

Plant-damaging insects
Heliothis armigera test

Active compound	Concentration in ppm	Kill in % after 6 ^d
triflumuron		
known	4	0
permethrin		
known	0.16	15
triflumuron + permethrin (25 : 1)		
according to the invention		
	4 + 0.16	<u>found</u> * <u>calc.</u> ** 40 15

* found = activity found

** calc. = activity calculated using Colby's formula

Example B

Phaedon cochleariae larvae test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

- 10 Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with larvae of the mustard beetle (*Phaedon cochleariae*) while the leaves are still moist.

After the desired period of time, the kill in % is determined. 100% means that all beetle larvae have been killed; 0% means that none of the beetle larvae have been killed. The determined kill rates are entered into Colby's formula (see sheet 1).

- 15 In this test, the following active compound combination in accordance with the present application showed a synergistically enhanced activity compared to the active compounds applied on their own:

Table B

Plant-damaging insects
Phaedon cochleariae larvae test

Active compound	Concentration in ppm	Kill in % after 3 ^d
triflumuron		
known	4	35
β-cyfluthrin		
known	0.16	15
triflumuron + β-cyfluthrin (25 : 1)		
according to the invention		
	4 + 0.16	<u>found</u> * <u>calc.</u> ** 55 44.75

* found = activity found

** calc. = activity calculated using Colby's formula

Table B

Plant-damaging insects
Phaedon cochleariae larvae test

Active compound	Concentration in ppm	Kill in % after 6 ^d
triflumuron		
known	4	65
deltamethrin		
known	0.16	50
triflumuron + deltamethrin (25 : 1)		
according to the invention		
	4 + 0.16	<u>found</u> * <u>calc.</u> ** 85 82.5

* found = activity found

** calc. = activity calculated using Colby's formula

Table B

Plant-damaging insects
Phaedon cochleariae larvae test

Active compound	Concentration in ppm	Kill in % after 3 ^d
<hr/>		
triflumuron		
known	4	25
<hr/>		
lambda-cyhalothrin		
known	0.16	15
<hr/>		
triflumuron + lambda-cyhalothrin (25 : 1)		
according to the invention		
		<u>found</u> * <u>calc.</u> **
	4 + 0.16	55 36.25
<hr/>		

* found = activity found

** calc. = activity calculated using Colby's formula

Example C

Spodoptera exigua test

Solvent: 7 parts by weight of dimethylformamide

Emulsifier: 2 parts by weight of alkylaryl polyglycol ether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvent and emulsifier, and the concentrate is diluted with emulsifier-containing water to the desired concentration.

- Cabbage leaves (*Brassica oleracea*) are treated by being dipped into the preparation of active compound of the desired concentration and are populated with caterpillars of the beet armyworm
10 (*Spodoptera exigua*) while the leaves are still moist.

After the desired period of time, the kill in % is determined. 100% means that all caterpillars have been killed; 0% means that none of the caterpillars have been killed. The determined kill rates are entered into Colby's formula (see sheet 1).

- In this test, the following active compound combination in accordance with the present application
15 showed a synergistically enhanced activity compared to the active compounds applied on their own:

Table C

Plant-damaging insects
Spodoptera exigua test

Active compound	Concentration in ppm	Kill in % after 6 ^d
triflumuron		
known	4	20
permethrin		
known	0.16	0
triflumuron + permethrin (25 : 1)		
according to the invention		
	4 + 0.16	<u>found</u> * <u>calc.</u> ** 30 20

* found = activity found

** calc. = activity calculated using Colby's formula

Example D

Critical concentration test/soil insects – treatment of transgenic plants

Test insect: *Diabrotica balteata* – larvae in soil

Solvent: 7 parts by weight of acetone

5 Emulsifier: 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent, the stated amount of emulsifier is added and the concentrate is diluted with water to the desired concentration.

10 The preparation of active compound is poured onto the soil. Here, the concentration of active compound in the preparation is virtually irrelevant, only the amount by weight of active compound per volume unit of soil, which is stated in ppm (mg/l), matters. The soil is filled in to 0.25 l pots and these are allowed to stand at 20°C.

15 Immediately after preparation, 5 pre-germinated maize corns of the variety YIELD GUARD (trademark of Monsanto Domp., USA) are placed into each pot. After 2 days, the test insects in question are placed into the treated soil. After a further 7 days, the efficacy of the active compound is determined by counting the maize plants that have emerged (1 plant = 20% efficacy).

Example E

Heliothis virescens test – treatment of transgenic plants

Solvent: 7 parts by weight of acetone

Emulsifier: 1 part by weight of alkylaryl polyglycol ether

- 5 To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amount of solvent and the stated amount of emulsifier, and the concentrate is diluted with water to the desired concentration.

- Soybean shoots (Glycine max) of the variety Roundup Ready (trademark of Monsanto Comp. USA) are treated by being dipped into the preparation of active compound of the desired
10 concentration and are populated with the tobacco batworm *Heliothis virescens* while the leaves are still moist.

After the desired period of time, the kill of the insects is determined.